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FROM VIRAL BARRIERS TO PROTON CONDUCTORS – NOVEL APPLICATIONS FOR POLYMERIC MEMBRANES

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Abstract
Novel applications for polymeric membranes which address the needs of health care industry and development of alternative energy sources are reviewed in this paper. Polyolefin membranes made by thermally-induced separation process can be used as barriers against biological pathogens and splashes of harmful liquid chemicals, or as separators in lithium ion batteries, which can provide an increased margin of safety by shutting down the electrical current in case of battery overheating. Asymmetric membranes made by a combination of immersion precipitation and photopolymerization can be used as proton exchange membranes in fuel cells. Modifications of this novel process could be used to make membranes for other interesting applications.

Introduction

A polymeric membrane represents a layer of polymeric material which serves as a selective barrier between two phases and shows preferential selectivity to some species in one of these phases when exposed to the action of a driving force. One of the earliest applications of polymeric membranes was blood purification by hemodialysis in the medical field. However, since the original invention of asymmetric membranes by Loeb and Sourirajan [1], the scope of applications for polymeric membranes has significantly expanded to include various treatments for purifying water sources using processes, such as reverse osmosis, ultrafiltration or microfiltration. Medical and water treatment applications represent today the largest business segments where commercial membranes are used, but other applications of polymeric membranes are slowly catching up.

This paper reviews some novel applications for polymeric membranes, which have emerged to address needs of the modern society, including better health care protection and substitution of traditional fossil fuel energy sources with alternative sources of energy. These applications focus either on membranes which serve as barriers against biological pathogens (bacteria, viruses) and harmful liquid chemicals, or on membranes used as separators in rechargeable lithium-ion batteries and proton conductors in fuel cells.

Barrier membranes

Barrier membranes are often produced on an industrial scale using thermally-induced phase separation (TIPS) process [2] schematically presented in Fig. 1. A semi-crystalline polymer and additives are dissolved in a diluent at high temperature, shaped into a film, cooled down to induce phase separation, followed by optional process steps of diluent extraction and film orientation to produce a microporous membrane. This membrane can be subjected to additional process steps to create the final product (e.g. coating, functionalization, lamination, winding). Fig. 2 illustrates thermodynamics of the phase separation process. At high temperatures polymer and diluent exist as a one phase solution and undergo phase separation by cooling down below the polymer crystallization curve (liquid-solid phase separation) or below the binodal equilibrium curve (liquid-liquid phase separation). After diluent removal and film orientation, a microporous membrane with a structure that is largely dependent on the type of phase separation process forms. Liquid-liquid phase separation creates a cellular microporous structure, while liquid-solid phase separation results in crystalline domains interconnected by polymer fibrils.

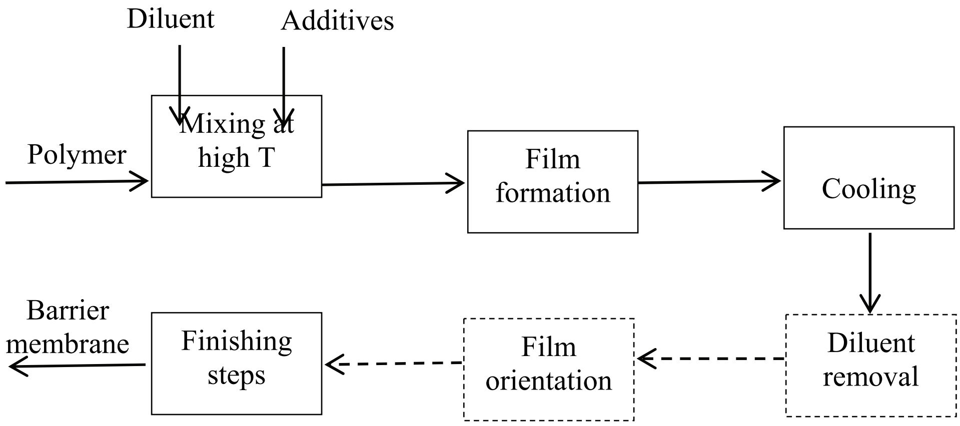

Figure 1. Schematic presentation of TIPS process to make barrier membranes.

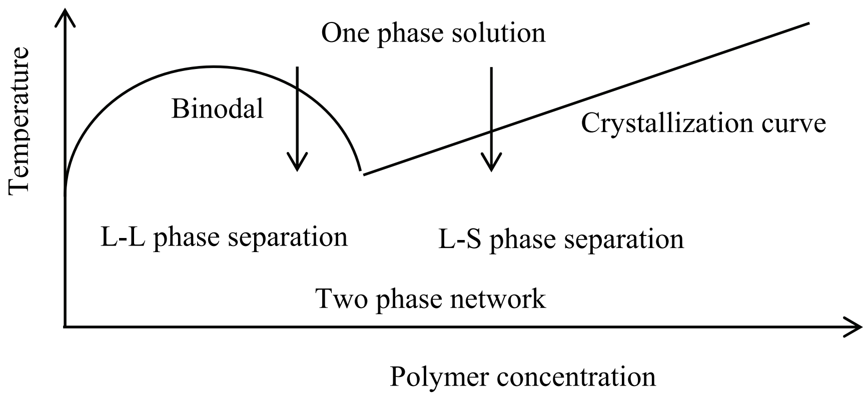

Figure 2. Schematic presentation of thermodynamics of the phase separation process.

If the polymer used in production has a sufficiently low surface energy, the resulting microporous membrane has a hydrophobic character and can serve as a barrier against liquids of higher surface tension (e.g. aqueous solutions). Liquid barrier conditions can be expressed by Laplace (Cantor) equation which determines the liquid breakthrough pressure when the membrane is pressurized with a nonwetting liquid :

$$P = \frac{4\gamma(-\cos\Theta)}{D} \qquad (1)$$

where γ is surface tension of liquid, D is the pore diameter of the membrane, and Θ is the contact angle between the membrane and the nonwetting liquid, which must be greater than 90^o, as shown in Fig. 3. Equation (1) shows that liquid barrier properties improve if the nonwetting liquid has a higher surface tension, the membrane has a smaller pore size, and the contact angle increases towards 180^o (membrane repellency against the liquid increases).

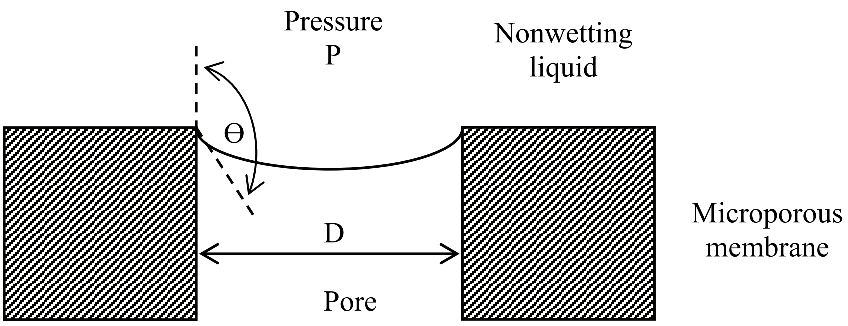

Figure 3. Liquid barrier conditions for a microporous film.

When a hydrophobic semicrystalline polymer, such as polypropylene or polyethylene is converted into a microporous membrane using TIPS process, membrane has a sufficient repellency against water to serve as a liquid barrier. However, liquids of lower surface tension readily penetrate such membranes even in the absence of pressure difference as driving force. A need to develop liquid barrier fabrics against liquids of lower surface tension than water (e.g. blood and body fluids, pesticide and herbicide spray solutions, organic solvents) led to a development of a new class of breathable microporous materials that are comfortable to wear, but still provide better protection against accidental splashes than standard protective garments. An example of such material used to prevent transmission of viruses from a patient to a health care worker is described in US patent literature [3, 4, 5, 6]. Several microporous membranes, in a film or laminate form, were prepared using TIPS process. The starting raw materials were polypropylene, mineral oil and fluorocarbon oxazolidinone (FCO) which improved barrier properties by increasing repellency (contact angle) against blood and body fluids compared to the control sample without FCO. These membranes were evaluated for viral penetration using an ASTM standard test method [7]. In this test a pressure of 13.8 KPa is applied to the test material through a liquid carrying viral pathogens and viral penetration is observed by swabbing the non- liquid-containing side of the test material, culturing the swabbed exudate for 24 hours, and counting the number of viruses. No viral penetration was typically detected using this test method when liquid repellency was sufficiently high (presence of FCO) and pore size was sufficiently small (TIPS polypropylene membranes). Breathable fabrics that can protect against viral penetration can find their use for surgical and emergency response garments. Liquid barrier properties of polyolefin membranes made by TIPS process can be further improved by coating these membranes with a curable fluorocarbon urethane composition, as described in [8]. Coated membranes were still quite breathable, while exhibiting repellency against liquids having surface tension above 20 dyne/cm (e.g. toluene, octane, ethyl acetate, isopropyl alcohol). Such materials could be useful as breathable industrial garments that can protect against splashes of organic solvents.

Lithium ion batteries exhibit high specific energy and long life power, which made them a source of choice for consumer electronic markets. The separator is a critical component in lithium ion batteries and it serves a dual purpose: physical separation of the battery electrodes and the safety function to shut down electrical current if overheating occurs, thus avoiding thermal runaway reactions that can lead to an explosion [9]. The separator needs to be thin and sufficiently porous to minimize electrical resistance of the electrolyte within its pores, mechanically strong and puncture resistant while having a small pore size to prevent internal shorts due to penetration of dendrites formed during the cycling operations. In addition, the separator needs to shut down the electrical current at a sufficiently low temperature. Commercial separators are usually made as a single or a multilayer structure comprising a polyethylene porous layer which melts in the range from 125 to 130^{o} C to block electrical current and stop battery overheating. Since this temperature range is rather close to the onset of exothermic runaway reactions that can occur in lithium ion batteries, significant efforts have been ongoing to develop a separator with a lower shutdown temperature and ensure an increased margin of safety. As described in patent literature, microporous membranes which meet all aforementioned requirements for the lithium ion battery separator application, while exhibiting a shutdown feature below 120^{o} C, can be made using TIPS process described in Fig. 1 [10, 11, 12]. It was shown that by using a compatible blend of polypropylene and ethylene alpha-olefin copolymer having crystallinity above 20% it was possible to prepare microporous films with a low temperature shutdown feature. Such separators can be used in lithium ion batteries as single layers, or multilayers made by co-extrusion. Fig. 4 shows a top view of a microporous film made by TIPS process, which could be useful as a battery separator. Scanning electron microscopy image of the top surface reveals a fine structure with pore sizes well below 100 nm.

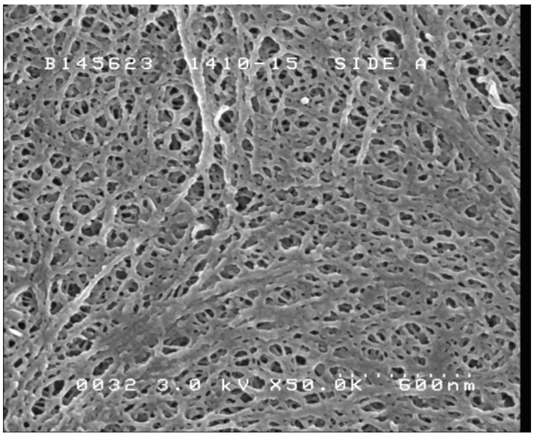

Figure 4. SEM image of a TIPS microporous membrane useful as lithium-ion battery separator [12].

Proton-conducting membranes

Fuel cells using proton exchange membranes have a broad range of applications in the automotive, stationary and portable fields [13]. In these fuel cells, a proton-conducting polymer membrane, such as Nafion available from DuPont de Nemours, serves as an electrolyte. High price of Nafion membranes and their limitations, including high crossover of methanol in Direct Methanol Fuel Cells and performance loss under conditions of low relative humidity, led to investigations of other proton-conducting membranes with interpenetrating networks from less expensive, nonfluorinated materials [14].

A novel method to make asymmetric membranes with interpenetrating proton-conducting morphology has been recently reported in literature [15]. This method, schematically shown in Fig. 5, combines traditional immersion precipitation process for making membranes and photopolymerization. A solution of polymer, monomers and photoinitiator in a common solvent is cast as a film on a glass plate, then immersed in a nonsolvent bath, quickly exposed to UV light to polymerize and crosslink monomers, and dipped in water to solidify the asymmetric structure. Polysulfone was used as polymer, while 2-acrylamido-2-methylpropane sulfonic acid (AMPS) was selected as a proton-conductive monomer. Final membrane had a thin skin layer with fine channels of crosslinked polyAMPS on top of a coarser support of interpenetrating polysulfone and polyAMPS phases.

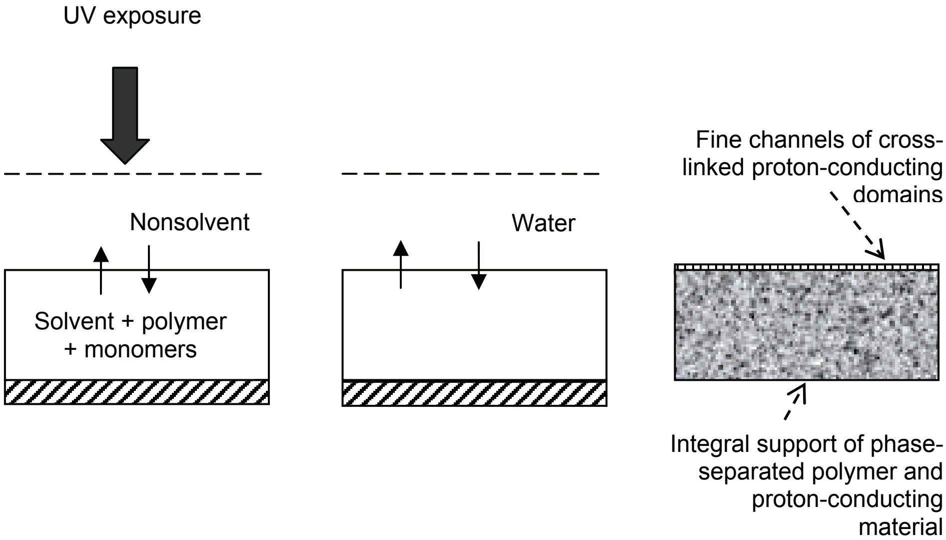

Figure 5. Schematic representation of the process for making an asymmetric membrane with interpenetrating proton- conducting morphology.

Environmental scanning electron microscope (ESEM) image of the top surface of an asymmetric proton-conducting membrane show crosslinked polyAMPS nanodomains of 200-300 nm average size. In-plane conductivity of such membrane, made with 5 mol % of a trifuncional crosslinking agent, was significantly higher than the conductivity of a Nafion 115 membrane, while having improved methanol barrier properties.

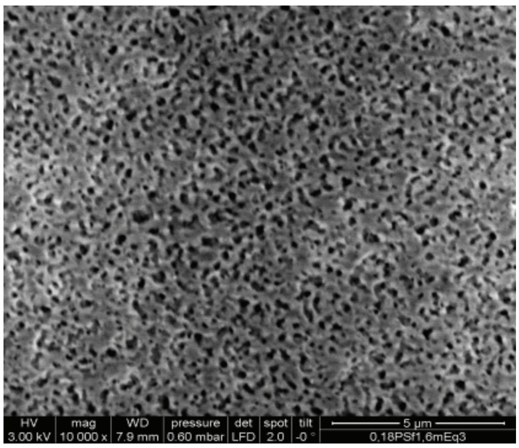

Figure 6. ESEM image of the top surface of an asymmetric membrane made by photopolymerization.

The new method of making asymmetric membranes with interpenetrating morphology is not necessarily restricted to fuel cell applications. Any polymerizable monomer soluble in the same solvent used for membrane casting could be incorporated, which significantly broadens the range of functional features that can be achieved with such materials. Current research in this area is looking into other potential applications, including low-pressure nanofiltration, gas separation and bio-applications using functionalized membranes.

Conclusion

Polypropylene membranes made by thermally-induced separation process can be used in many applications as barrier membranes. Their barrier properties are improved by increasing repellency against contacting liquid and by reducing their pore size. Such properties can lead to their use in garments protecting against biological pathogens and splashes of harmful liquid chemicals. Polyolefin membranes made by thermally-induced phase separation process can also be used as separators in lithium ion batteries, where they can provide an increased margin of safety by their thermal shutdown feature.

Asymmetric membranes made by a combination of immersion precipitation and photopolymerization have exhibited electrical conductivity significantly higher than that of a Nafion 115 membrane, while having improved methanol barrier properties. Such membranes can be useful as proton conductors in fuel cells. Modifications of this novel process for making membranes could also be used to develop membranes for other interesting applications.

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